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		56	Prior art references: DE 1 95 14 202 A1 EP 07 03 188 A1 EP 06 81 989 A1 WO 90 14 307 Ullmanns Enzyklopädie der technischen Chemie, 4. Aufl., Bd. 18, S. 653, Bd. 21, S. 464, 467, 469-471 [Ullmann's Encyclopedia of Chemistry Engineering]

The following details have been taken from the documents handed in by the applicant.

The Application for Examination has been filed according to § 44 of the Patents Law.

54 Doped pyrogenically made oxides

55 Pyrogenically made metal and/or non-metal oxides doped with one or several doping constituents of 0,00001 – 20 per cent in weight. The doping constituent may be metal and/or nonmetal or oxide and/or metal or nonmetal salt. The doped oxide BET surface may range between 5-600 m²/g.

metal and/or nonmetal compounds by adding to the gas mixture an aerosol containing a hydrous metal and/or nonmetal.

Doped pyrogenically made oxides may be used, for instance, as loading material.

Doped pyrogenically made metal and/or nonmetal oxides are manufactured by means of flame hydrolysis of vaporisable



This invention is related to doped pyrogenically made oxides, the process of their manufacturing as well as their use.

It is known that doped pyrogenically made oxides may be loaded with metal salts or metal oxides by first mixing pyrogenically made oxides with hydrous metal salt solutions and, subsequently, drying or calcining them. The disadvantages of products manufactured in such processes are a): the doping body is not evenly distributed all over the primary particle or b): depending on the kind of doping, non-homogeneities may occur in the compound. Hence it is possible that, after doping and calcining, the doping body's primary particles may be separated and appear to be much larger in diameter than the primary particles of the pyrogenic oxides.

Therefore the objective was to homogeneously dope pyrogenically made oxides with another matter and, at the same time, to avoid that primary particles of the doping agents or, respectively, its oxides occur separately from the primary particles of the pyrogenically made oxide.

The subject matter of invention are doped pyrogenically made metal or nonmetal oxides characterised as follows: they are basic constituents of pyrogenically – in a flame hydrolysis process – made metal or nonmetal oxides doped with at least one doping constituent of 0,00001-20 percent in weight, with a doping agent quantity preferably ranging between 1 and 10 000 ppm, the doping constituent being a nonmetal and/or metal, or a nonmetal and/or metal salt, or a metal and/or nonmetal oxide, and the doped oxide BET surface ranging between 5 and 600 m²/g.

Another subject matter of invention is a process of production of doped pyrogenically made metal and/or nonmetal oxides which is described as follows: an aerosol is fed into such a flame as is used for the production of pyrogenic oxides in the known flame hydrolysis process. Prior to reaction, this aerosol is homogeneously mixed with the flame oxidation or flame hydrolysis gas mixture. Then the aerosol-gas mixture is allowed to complete reaction in a flame, and the resulting pyrogenically made oxides are separated from the gas flow in the commonly known way. In this process, the initial product used as aerosol is a salt solution or suspension containing the constituent to be doped, which may consist in a metal or nonmetal salt or a mixture of both, or in a suspension of insoluble metal or non-metal compounds. It is manufactured preferably using the ultrasonic method with a two-component nozzle or an aerosol generator.

In one of the preferred designs of the invention, the aerosol is supplied using devices like the one shown in Fig. 1. The gas and aerosol feeder lines may be interchanged.

In another design of the invention, the aerosol can be supplied using a concentric nozzle preferably placed in a position perpendicular with the main gas flow.

The nonmetals/metals aluminium, niobium, titanium, wolfram, zircon, germanium, boron, and/or silicon can be used as basic constituent.

Metals/nonmetals and their compounds, if liquid soluble or suspensible, may be used as doping constituents. In one of the preferred designs of the invention, compounds of transition metals and/or noble metals can be used.

For example, it is possible to use cerium or potassium salts as doping constituents.

The flame hydrolysis process is known from Ullmann's Enzyklopädie der technischen Chemie, 4. Auflage, Band 21, Seite 464.

Due to the fine doping constituent dispersion in the aerosol and the high process temperature (1000 – 2400°C) in the subsequent flame hydrolysis, during which the doping constituents, depending on the circumstances, are further comminuted or molten, the doping fluid is finely dispersed in the gaseous phase. Thus the doping constituent can be homogeneously integrated into the pyrogenically made oxide.

The process designed according to invention allows to dope all known pyrogenically made oxides (e. g. SiO_2 , TiO_2 , Al_2O_3 , B_2O_3 , ZrO_2 , GeO_2 , WO_3 , Nb_2O_5) with other metals or metal oxides or their compounds.

The process designed according to invention has several advantages: selecting the appropriate doping constituents one can influence the aggregate or, respectively, agglomerate structure of the pyrogenic oxide.

Apart from this, the process allows to influence the pH of the pyrogenic oxide.

Catalytically active matters, such as cerium or noble metals, used as doping constituents can be almost homogeneously dispersed in the pyrogenically made oxide.

Doping also allows to influence phase transformation (e. g. from rutile to anatase) in pyrogenically made oxides.

The process designed according to invention allows to combine pyrogenically made oxide properties, which until now could either not be achieved at all or in multi stage processes only.

Pyrogenically made metal/nonmetal oxides produced according to invention can be used as loading materials, base materials, catalytically active matter, starting material in dispersion production, polishing agents for the finishing of metal or silicon disks in electric industries (CMP applications), basic ceramic materials in electronics and cosmetics industries, as additives in silicone and rubber industries, for rheological conditioning in fluid systems, for heat protection stabilisation, as heat insulators in lacquer industries etc.

Another subject matter of invention consists in a device to run the process according to invention. It is characterised by a (preferably aligned) aerosol feeder tube ending right before the burner nozzle.

The burner lay-out used in examples 1-4 is schematically shown in Fig. 1.

According to Fig. 1, the core of the device is the burner 1 of known design as commonly used to produce pyrogenically made oxides.

The burner 1 is composed of the central tube 2 discharging and burning the main flow of gas in the combustion space. The internal nozzle is enclosed in an additional ring nozzle (shroud nozzle) emitting protective or secondary hydrogen in order to avoid slag baking.

According to invention, the central tube 2 contains the axial tube 5 ending a few centimetres right before the nozzle 3 of the central tube 2. The aerosol is fed into the axial tube 5, and the aerosol-gas flow from axial tube 5 is homogeneously mixed with the flow of gas of central tube 2 in the final segment of the latter.

The aerosol is generated in the aerosol generator 6 (ultrasonic atomizer). The aerosol educt used in this process is an aqueous salt solution containing the metal/nonmetal in the form of solved or dispersed/suspended salt.

The aerosol generated in the aerosol generator 6 is transferred in a flow of carrier gas through the heating area 6, where the water evaporates and small salt crystals remain finely dispersed in the gaseous phase.

Example 1 (no doping)

4,44 kg/h SiCl_4 are vaporised at approx. 130°C and then fed into the central pipe of the burner. In addition, $3 \text{ Nm}^3/\text{h}$ of primary hydrogen and $8,0 \text{ Nm}^3/\text{h}$ of air are fed in. The gas mixture is emitted through the central burner nozzle to flame into the combustion space and the adjacent water-cooled flame tube.

The ring nozzle surrounding the central nozzle is supplied with $0,5 \text{ Nm}^3/\text{h}$ of protective or secondary hydrogen in order to avoid slag baking on the nozzles.

In addition, $12 \text{ Nm}^3/\text{h}$ of secondary air are fed into the combustion space.

Out of the axial tube, the aerosol flows into the central tube. The aerosol consists of 195 g/h water vapour generated in the aerosol generator from pure distilled water in an ultrasonic atomising process.

The atomised water vapour is transferred through a heated conduct by a carrier gas consisting of $0,5 \text{ Nm}^3/\text{h}$ of air, and the aerosol transforms into gas at a temperature of 180°C .

The temperature of the gas mixture (SiCl_4 -air-hydrogen or, respectively, water-aerosol) is 150°C at the burner head (nozzle 3).

The reaction gases and the pyrogenic silicic acid generated are sucked through a cooling system by negative pressure applied to the flame tube and thereby cooled down to approx. $100\text{-}160^\circ\text{C}$. The solid matter is separated from the exhaust gas flow by means of a filter or cyclone.

The silicic acid occurs in the form of a fine grained white powder. In a subsequent process step, the silicic acid is treated at an increased temperature with steamy air to remove the adherent remains of hydrochloric acid.

The BET surface of the pyrogenic silicic acid is $150 \text{ m}^2/\text{g}$.

The process parameters are given in Table 1. Additional analytical data on the pyrogenic silicic acid generated are indicated in Table 2.

Example 2 (doping with cerium.)

The procedure is the same as indicated in example 1:

$4,44 \text{ kg/h}$ SiCl_4 are vaporised at approx. 130°C and then fed into the central pipe of the burner. In addition, $3 \text{ Nm}^3/\text{h}$ of primary hydrogen and $8,0 \text{ Nm}^3/\text{h}$ of air are fed in. The gas mixture is emitted through the central burner nozzle to flame into the combustion space and the adjacent water-cooled flame tube.

Examples

The ring nozzle surrounding the central nozzle is supplied with 0,5 Nm³/h of protective or secondary hydrogen in order to avoid slag baking on the nozzles.

In addition, 12 Nm³/h of secondary air are fed into the combustion space.

Out of the axial tube, the aerosol flows into the central tube. The aerosol consists of 210 g/h of a cerium salt aerosol generated from a 5 percent aqueous cerium(III)-chloride-solution in an ultrasonic atomising process.

The cerium salt aerosol is transferred through a heated conduct by a carrier gas consisting of 0,5 Nm³/h of air, and the aerosol transforms into gas and a salt crystal aerosol at a temperature of approx. 180°C.

The temperature of the gas mixture (SiCl₄-air-hydrogen, aerosol) is 180°C at the burner head.

The reaction gases and the cerium doped silicic acid generated are sucked through a cooling system by negative pressure applied to the flame tube and thereby cooled down to approx. 100-160°C. The solid matter is separated from the exhaust gas flow by means of a filter or cyclone.

The doped pyrogenically made silicic acid occurs in the form of a fine grained white powder. In a subsequent process step, the silicic acid is treated at an increased temperature with steamy air to remove the adherent remains of hydrochloric acid.

The BET surface of the pyrogenic silicic acid is 143 m²/g.

The process parameters are given in Table 1. Additional analytical data on the pyrogenic silicic acid generated are indicated in Table 2.

Example 3 (no doping)

4,44 kg/h SiCl₄ are vaporised at approx. 130°C and then fed into the central pipe of the burner. In addition, 3 Nm³/h of primary hydrogen and 8,7 Nm³/h of air are fed in. The gas mixture is emitted through the central burner nozzle to flame into the combustion space and the adjacent water-cooled flame tube.

The ring nozzle surrounding the central nozzle is supplied with 0,5 Nm³/h of protective or secondary hydrogen in order to avoid slag baking on the nozzles.

In addition, 12 Nm³/h of secondary air are fed into the combustion space.

Out of the axial tube, the aerosol flows into the central tube. The aerosol consists of 210 g/h water vapour generated in the aerosol generator from pure distilled water in an ultrasonic atomising process.

The aerosol is transferred through a heated conduct by a carrier gas consisting of 0,5 Nm³/h of air, and it transforms into gas at a temperature of 180°C.

The temperature of the gas mixture (SiCl₄-air-hydrogen, water vapour or, respectively, water-aerosol) is 180°C at the burner head.

The reaction gases and the pyrogenic silicic acid generated are sucked through a cooling system by negative pressure applied to the flame tube and thereby cooled down to approx. 100-160°C. The solid matter is separated from the exhaust gas flow by means of a filter or cyclone.

The silicic acid occurs in the form of a fine-grained white powder. In a subsequent process step, the silicic acid is treated at an increased temperature with steamy air to remove the adherent remains of hydrochloric acid.

The BET surface of the pyrogenic silicic acid is 215 m²/g.

The process parameters are given in Table 1. Additional analytical data on the pyrogenic silicic acid generated are indicated in Table 2.

Example 4 (doping with cerium)

The procedure is the same as indicated in example 1:

4,44 kg/h SiCl_4 are vaporised at approx. 130°C and then fed into the central pipe of the burner. In addition, $3 \text{ Nm}^3/\text{h}$ of primary hydrogen and $8,7 \text{ Nm}^3/\text{h}$ of air are fed in. The gas mixture is emitted through the central burner nozzle to flame into the combustion space and the adjacent water-cooled flame tube.

The ring nozzle surrounding the central nozzle is supplied with $0,5 \text{ Nm}^3/\text{h}$ of protective or secondary hydrogen in order to avoid slag baking on the nozzles.

In addition, $12 \text{ Nm}^3/\text{h}$ of secondary air are fed into the combustion space.

Out of the axial tube, the aerosol flows into the central tube. The aerosol consists of 205 g/h of a cerium salt aerosol generated from a 5 percent aqueous cerium(III)-chloride-solution in an ultrasonic atomising process.

The cerium salt aerosol is transferred through a heated conduct by a carrier gas consisting of $0,5 \text{ Nm}^3/\text{h}$ of air, and the aerosol transforms into gas and a salt crystal aerosol at a temperature of approx. 180°C .

The temperature of the gas mixture (SiCl_4 -air-hydrogen, aerosol) is 180°C at the burner head.

The reaction gases and the cerium doped silicic acid generated are sucked through a cooling system by negative pressure applied to the flame tube and thereby cooled down to approx. $100\text{-}160^\circ\text{C}$. The solid matter is separated from the exhaust gas flow by means of a filter or cyclone.

The doped pyrogenically made silicic acid occurs in the form of a fine grained white powder. In a subsequent process step, the silicic acid is treated at an increased temperature with steamy air to remove the adherent remains of hydrochloric acid.

The BET surface of the pyrogenic silicic acid is $217 \text{ m}^2/\text{g}$.

The process parameters are given in Table 1. Additional analytical data on the pyrogenic silicic acid generated are indicated in Table 2.

Example 5 (doping with potassium salts)

The procedure is the same as indicated in example 1, the salt solution used being a 0,5 percent aqueous potassium chloride solution.

4,44 kg/h SiCl_4 are vaporised at approx. 130°C and then fed into the central pipe of the burner. In addition, $3 \text{ Nm}^3/\text{h}$ of primary hydrogen and $8,7 \text{ Nm}^3/\text{h}$ of air are fed in. The gas mixture is emitted through the central burner nozzle to flame into the combustion space and the adjacent water-cooled flame tube.

The ring nozzle surrounding the central nozzle is supplied with $0,5 \text{ Nm}^3/\text{h}$ of protective or secondary hydrogen in order to avoid slag baking on the nozzles.

Out of the axial tube, the aerosol flows into the central tube. The aerosol consists of 215 g/h of a potassium salt aerosol generated from a 5 percent aqueous cerium(III)-chloride-solution in an ultrasonic atomising process.

The potassium salt aerosol is transferred by a carrier gas consisting of $0,5 \text{ Nm}^3/\text{h}$ of air through a heated conduct, and the aerosol transforms into gas and a salt crystal aerosol at a temperature of approx. 180°C .

The temperature of the gas mixture (SiCl_4 -air-hydrogen, aerosol) is 180°C at the burner head.

The reaction gases and the potassium doped silicic acid generated are sucked through a cooling system by negative pressure applied to the flame tube, and flow of particles and gas is cooled down to approx. $100\text{-}160^\circ\text{C}$. The solid matter is separated from the exhaust gas flow by means of a filter or cyclone.

The doped pyrogenically made silicic acid occurs in the form of a fine grained white powder. In a subsequent process step, the silicic acid is treated at an increased temperature with steamy air to remove the adherent remains of hydrochloric acid.

The BET surface of the pyrogenic silicic acid is 199 m²/g.

The process parameters are given in Table 1. Additional analytical data on the pyrogenic silicic acid generated are indicated in Table 2.

Table 1
Experimental conditions in doped pyrogenic silicic acid production

No.	SiCl ₄ kg/h	Primary air Nm ³ /h	Sec. air Nm ³ /h	H ₂ Core Nm ³ /h	H ₂ Prot. Nm ³ /h	N ₂ Prot. Nm ³ /h	Gas temp. C°	Salt solution	Aerosol quantity kg/h	Air aerosol Nm ³ /h	BET m ² /g
Doped with cerium salt and other examples for comparison											
1	4,44	8,0	12	3	0,5	0,3	150	H ₂ O only	0,195	0,5	150
2	4,44	8,0	12	3	0,5	0,3	180	5%CeCl ₃	0,210	0,5	143
3	4,44	8,7	12	3	0,5	0,3	180	H ₂ O only	0,210	0,5	215
4	4,44	8,7	12	3	0,5	0,3	180	5%CeCl ₃	0,205	0,5	217
Doped with potassium salt and other examples for comparison											
3	4,44	8,7	12	3	0,5	0,3	180	H ₂ O only	0,210	0,5	215
5	4,44	8,7	12	3	0,5	0,3	180	0,5%KCl	0,215	0,5	199

OTES: Primary air = Air quantity in central tube; Sec. air: secondary air; H₂-core = Hydrogen in central tube; Gas temp. C° = Gas temperature at central pipe nozzle; Aerosol quantity = Mass flow rate of salt solution transformed into aerosol; Air aerosol = quantity of carrier gas (air) used to transfer aerosol

able 2

analytical data found in the samples obtained in examples 1 – 5

No.	BET [m ² /g]	Ce mass µg/g	K mass µg/g	Cl- content ppm	LD mass %	LB mass %	Cl ppm	Grindo meter µm	Sedi - Vol %	Efficien cy	pH 4% sus.	Tampe d den- sity g/l	Thicken ing in Ludopa I [mPas]
Doped with cerium salt, examples for comparison													
1	150	–			0,19	1,29		18	0	697	3,98	27	1745
2	143	1860	< 5		0,09	0,09		20	0	690	3,39	26	1990
3	215	84	< 5	45	0,27	0,27	45	18	11	422	4,00	25	3390
4	217	2350	< 5	112	0,22	0,22	112	40	50	548	3,67	29	3680
Doped with potassium salt, examples for comparison													
3	215		< 5	45	0,27	0,27	45	18	11		4,00	25	3390
5	199		300	55	0,32	0,32	55	60	50		4,83	32	2575

NOTES: Cerium content indicated in Ce in µg (ppm); Potassium content in K in µg (ppm); LD = loss due to drying; (2h at 105°C following DIN/ISO787/II, ASTM D 280, JIS K 5101/21); LB = loss due to burning (2h at 1000°C following DIN 55921, ASTM D 208, JIS K 5101/23 with reference to the aforementioned 2h at 105°C for dried matter); Grindometer = grindometric value; Sedimentation = volume of sediment; Efficiency = turbidimetry; the efficiency determination method (turbidimetry) is described in Patent specification DE 44 00 170; the suspension manufactured following the same method is used to determine sediment volume after

waiting time of another 5 minutes; tamped density is determined following DIN/ISO 787/IX, JIS K 5101/18 (non-sifted). Thickening in polyester reference system: described in EP-A 0 015 315

Fig. 2 shows an EM micrograph of pyrogenic silicic acid made as indicated in example 3 (no doping).

Fig. 3 shows an EM micrograph of pyrogenic silicic acid made as indicated in example 4 (doping with cerium salt).

It is obvious that doping with cerium salt changes the structure of the aggregate or, respectively, the conglomerate. Doping generates larger coherent structures.

The analytical data found in silicic acid (example 4) show a larger sediment volume and significantly improved efficiency values by comparison with the silicic acid data in example 3. This also indicates an enlargement of the aggregate or, respectively, conglomerate structure.

In addition, it is possible to achieve a significant improvement of thickening in unsaturated polyester resins when using silicic acid doped with cerium according to this invention.

Patent Claims

1. Doped pyrogenically made metal and/or nonmetal oxides with the **following characteristics**: Their basic constituents are pyrogenically, i.e. in a flame hydrolysis process, made metal and/or nonmetal oxides doped with at least one doping constituent of 0,00001 – 20 percent in weight, the doping quantity ranging preferably between 1 and 10,000 ppm. The doping constituent is a nonmetal and/or metal or a salt/oxide of a metal/nonmetal. The BET surface of the doped oxides ranges between 5 and 600 m²/g.
2. Process to manufacture pyrogenically made oxides of metals and/or nonmetals with the **following characteristics**: an aerosol is fed into such a flame as is used for the production of pyrogenic oxides in the known flame hydrolysis process. Prior to reaction, this aerosol is homogeneously mixed with the flame oxidation or flame hydrolysis gas mixture. Then the aerosol-gas mixture is allowed to complete reaction in a flame, and the resulting pyrogenically made oxides are separated from the gas flow in the commonly known way. In this process, the initial product used as aerosol is a salt solution or suspension containing the constituent to be doped, which may consist in a metal or non-metal salt or a mixture of both, or in a suspension of insoluble metal or non-metal compounds. It is manufactured preferably using the ultrasonic method with a two-component nozzle or an aerosol generator.
3. According to claim 1, doped pyrogenically made oxides can be used as loading materials, base materials, catalytically active matter, starting material in dispersion production, polishing agents for the finishing of metal or silicon disks in electric industries (CMP applications), basic ceramic materials in electronics and cosmetics industries, as additives in silicone and rubber industries, for rheological conditioning in fluid systems, for heat protection stabilisation, as heat insulators in lacquer industries etc.
4. A device to run the process according to claim 2 with the **following characteristics**: A burner of known design used to manufacture pyrogenically made oxides contains a (preferably aligned) aerosol feeder tube ending right before the burner nozzle.

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See 3 pages of drawings

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